Tungsten(0) and rhodium(I) complexes of a series of 2-(2′-halo)triarylphosphinines

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A series of halo substituted triarylphosphinines have been synthesised and coordinated to tungsten(0) and rhodium(I) to give [(2-(2′-halo)-triarylphosphinine)$W(CO)_5$] and [(2-(2′-halo)-triarylphosphinine)Rh(COD)Cl] respectively. The complexes have been examined by NMR and IR spectroscopy in an effort to elucidate the nature of the bonding between the phosphinines and the respective metal centre. The $W(CO)_5(L)$ systems reveal restricted C–C bond rotation as evidenced by temperature-dependent $^{31}P\{^1H\}$ NMR spectra. Thermodynamic barriers to the rotation are dependent upon the nature of the halide with $\Delta G^{\ddagger}$ values of 72.5 kJ mol^{-1} and 50.8 kJ mol^{-1} being obtained for the chloro- and fluoro-derivatives, respectively; activation barriers for the iodo- and bromo- derivatives were beyond the accessible temperature range of the NMR experiment.

Introduction

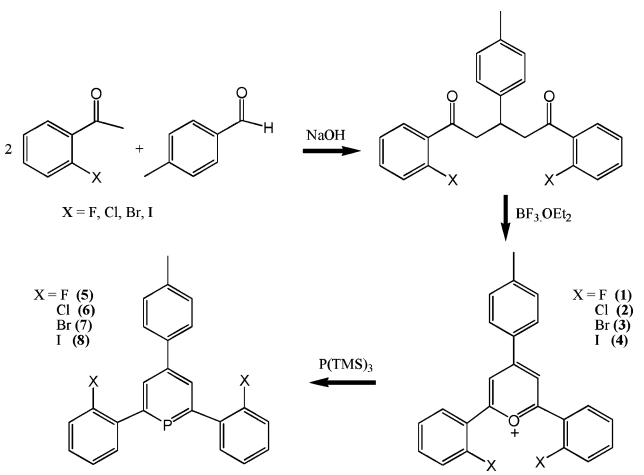
Over the last few years the synthesis, coordination chemistry and catalytic properties of phosphinines have been investigated by various groups.[1] These broad-ranging studies include the development of new synthetic routes,[2] through the preparation of functionalised phosphinines,[3] to the generation of phosphinine anions.[4] Intrinsic to all these investigations has been a desire to evaluate the properties of the phosphinines in order to establish the nature of this donor type with regard to more traditional P-donors such as phosphines and phosphites. A concise account of phosphinine chemistry up to 2007 is given in the review by Müller and Vogt.[5] Reported phosphinines include SPS pincer ligands,[6] heterodonor phosphino-phosphinines,[7] tripodal phosphinines[8] and macrocycles.[9] Most of these studies highlight the fact that phosphinines behave as good π-acceptors but relatively poor σ-donors; this latter property relates to the contracted lone pair which is the $HOMO^{-2}$ in phosphinines.

The strong π-acceptor nature of the phosphinines has attracted interest from groups concerned with homogeneous catalysis. In the area of hydroformylation, for example, phosphinines have been touted as replacements for π-acceptor ligands such as phosphites which are known to be good for stabilizing the low oxidation states of the metal during the catalytic cycle. Much of the impetus for the investigation of these heterocyclic phosphines stems from a desire to supplant phosphites and phosphonites (which are prone to decomposition under catalytic conditions) with more robust ligands that mimic or better the performance of the $P(OR)_3/RP(OR')_2$ systems.[10]

Even though triarylphosphinines are relatively common (2,4,6-triphenyl phosphinine being the most widely used), systems containing other heteroatoms, particularly potentially reactive groups such as halide that may allow further functionalisation have not appeared. As part of our interest in heterocyclic and macrocyclic phosphorus donors we sought a route to 2,2′-dihalo-substituted arylphosphinines for two main purposes. The first was to study their basic coordination properties in order to establish whether such ligands behave in a similar manner to the unsubstituted analogues and the second, longer-term aim, was a view to developing further functionalised systems. The current paper deals with aspects of the coordination chemistry of the dihalo substituted arylphosphinines highlighting similarities and differences between the current ligands, their unsubstituted analogues and phosphines in general.

Results and discussion

Compounds **1–4** were synthesised *via* a variation of a literature procedure.[11] The series of halide substituted pyrylium salts, which are reported here for the first time, were obtained as air- and moisture-stable, bright yellow solids in yields ranging from 5% to 89% (Scheme 1). The very low yield for the iodo derivative (5%) is somewhat anomalous, but it is not known why the



Scheme 1

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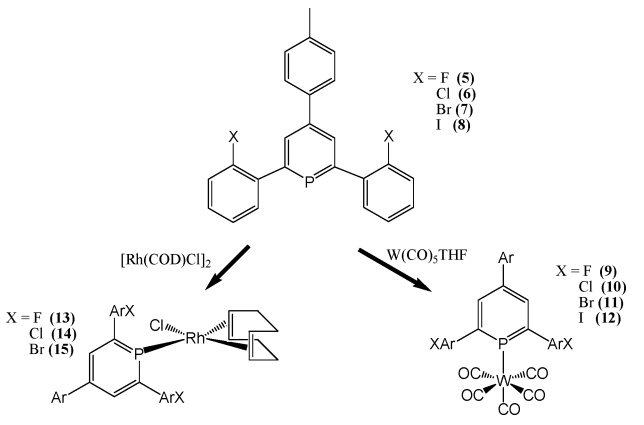
isolated yield was so low. The corresponding phosphinines **5–8** were synthesised using a methodology introduced by Maerkl[12] and further developed by Breit to negate the use of phosphine gas.[10] Thus, compounds **5–8** were synthesised from their respective pyrylium salt by reaction with 2 equivalents of $P(SiMe_3)_3$ in refluxing dimethoxyethane in yields ranging from 27% to 63%. The use of DME is preferred to the acetonitrile originally used by Maerkl as cleaner reactions were observed with the former solvent; only the phosphinine and, on occasion, unreacted tris(trimethylsilyl)phosphine were observed in the $^{31}P\{^1H\}$ NMR spectra of the reaction mixtures after reflux. Excess $P(SiMe_3)_3$was removed as PH_3 after decomposition with methanol at room temperature. The phosphinines were all characterised by NMR spectroscopy and high resolution mass spectrometry, and are, to the best of our knowledge, the first reported phosphinines of their type. The compounds are orange solids that can be crystallised as feathery 'herring bone' type crystals, that were unsuitable for analysis by single-crystal X-ray crystallographic techniques. Comparison of the $^{31}P\{^1H\}$, ^1H and $^{13}C\{^1H\}$ spectra for the phosphinines **5–8** reveals little difference in the spectra across the series. The $^{31}P\{^1H\}$ chemical shifts lie in a narrow range from 192.2 to 193.1 ppm and the ^1H NMR spectra are dominated by aromatic resonances which often overlap making individual assignment difficult. The carbon atoms adjacent to the phosphorus atom in the phosphinine ring show little change in either shift or coupling constant across the halophosphinine series. The only notable difference is in compound **5** were the C-2′ carbon is clearly distinguished by its coupling to the fluorine atom.

Compounds **9–12** (Scheme 2) were made by reacting the appropriate halo-arylphosphinine with $W(CO)_5THF$ (made *in situ* by the photolysis of $W(CO)_6$ in THF) at room temperature. The resulting phosphinine–tungsten complexes, $W(CO)_5(L)$, were fully characterised by NMR spectroscopy and high resolution mass spectrometry. Unlike with the majority of tertiary phosphines, the coordination induced shifts ($\Delta\delta_P$) are upfield for phosphinines, an anomaly partly ascribed to the phosphorus atom being a sp^2 centre compared to sp^3 in a typical tertiary phosphine. The chemical shifts in the ^{31}P NMR spectra of the tungsten–phosphinine complexes (**9–12**) are similar to related complexes reported by Mathey and co-workers,[13] where upfield shifts are observed upon coordination albeit to a lesser extent than those observed here. This is not surprising as the phosphinines of Mathey are significantly different to the current ligands.



Scheme 2

The electronic changes at the phosphorus centre induced upon coordination are not only evident in the ^{31}P NMR chemical shifts, but also in the absolute value of the coupling constants in the ^1H and $^{13}C\{^1H\}$ NMR spectra. In particular, the protons of the C-3 and C-5 positions on the phosphinine ring experience a change in the $^2J_{H-P}$ coupling constant from around 6 Hz to >17 Hz and the $^1J_{C-P}$ coupling constants to the C-2 and C-6 carbons adjacent to the phosphorus atom decrease from around 52 Hz to 15 Hz upon coordination.

An interesting feature of these complexes arises in the ^{31}P NMR spectra where for the chloro-, bromo- and iodo- derivatives, two peaks of unequal intensity are observed at room temperature. This observation is tentatively assigned to the presence of two rotameric isomers resulting from restricted P–C bond rotation as a consequence of the bulk of the halide: the fluoro-derivative, **9**, shows only one peak in the $^{31}P\{^1H\}$ NMR spectrum at room temperature (see later). The two possible rotamers are assigned as *cis* and *trans* according to the relative orientation of the halo-aryl groups. The two peaks observed at room temperature in the $^{31}P\{^1H\}$ NMR spectrum of the chloro-derivative were observed to coalesce upon heating to 388 K, enabling the activation energy of 72.5 kJ mol^{-1} for this rotation barrier to be determined. For the bromo-, and iodo- derivatives however, coalescence was not observed upon heating to 110 °C indicating, as expected, substantially higher rotation barriers for these bulkier analogues. Variable temperature $^{31}P\{^1H\}$ NMR spectroscopic studies of the fluoroarylphosphinine complex **9**, which gives a singlet at room temperature, revealed the presence of two signals for the two rotamers at low temperature (258 K, Fig. 1). Upon warming these two resonances coalesce allowing the activation barrier of 50.8 kJ mol^{-1} to be determined. The equilibrium constant between rotamers did not appear to be temperature dependent as the ratios of the peaks in the ^{31}P spectra remained constant (approximately 1:2). It seems reasonable to suggest that the major rotamer is the *trans* isomer, as this would provide the greater steric relief in the complex. The presence of two rotamers, leads to broadening and this coupled with extensive overlap of peaks in the aromatic region of the ^1H NMR spectra of the complexes makes unequivocal assignment of the peaks difficult to the extent that full assignment was not possible in all cases. Similar problems were encountered in the $^{13}C\{^1H\}$ NMR spectra.

The IR spectra of the phosphinine–tungsten complexes gives insight into the nature of the W–P bond as the carbonyl stretching frequencies are sensitive to the electronic nature of the phosphinine ligands. Table 1 compares the current complexes with other phosphorus based ligand complexes of pentacarbonyltungsten(0). As can be seen from Table 1, the phosphinines are most closely similar to alkyl and aryl phosphites on this basis and in agreement with the observations of Kozlowski *et al.*[16] Although there seems to be no difference between the iodo-, bromo-, and chloro- derivatives, there is a small increase in the stretching frequencies with the fluoro- derivative indicating increased π-acceptor behaviour as might be expected with the enhanced electronegativity of the halide. The major and minor rotamers in compounds **10–12** appear indistinguishable in the IR spectra, as only the three carbonyl stretches expected for a $M(CO)_5(L)$ complex are observed. The $^1J_{P-W}$ coupling constants for all the tungsten complexes were 281 Hz (Table 2). This compares with the value of 280 Hz for $W(CO)_5(PPh_3)$,[17] but is significantly smaller than that of 404 Hz

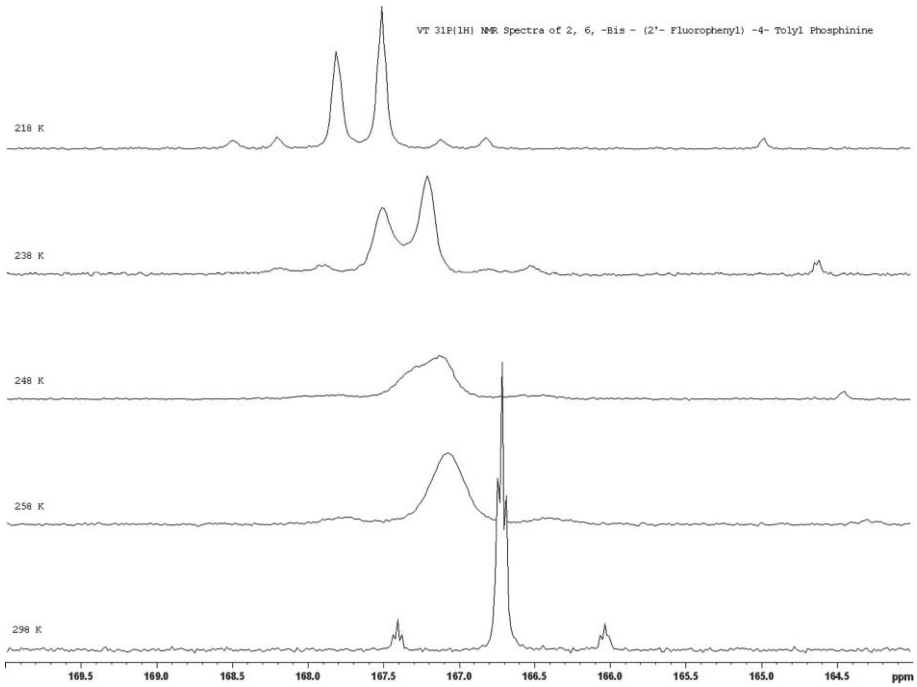


Fig. 1 Variable temperature NMR study of the 2-fluorophosphinine complex, **9**.

Table 1 Carbonyl stretching frequencies for complexes **9–12** and related systems

	ν(CO) cm^{-1}			
L	A_1^2	A_1^1	E	Ref.
$P(NMe_2)_3$	2067	1942	1933	14
PMe_3	2069	1949	1939	14
PPh_3	2071	1942	1942	15
$P(OMe)_3$	2079	1962	1948	15
12	2076	1983	1954	
11	2076	1983	1954	
9	2076	1983	1954	
9	2077	1981	1959	
$P(OPh)_3$	2083	1968	1959	14
$P(CF3)_3$	2101	2006	1998	15

observed in $W(CO)_5\{P(OPh)_3\}$.[18] Thus this data would appear to support the notion that the current phosphinines are closely similar to PPh_3 in their bonding properties and taking the NMR and IR spectroscopic data into account, it is reasonable to suggest that the σ-donor/π-acceptor properties of these phosphinines lie closer to those of PPh_3 than $P(OPh)_3$.

Complexes **13–15** were synthesised by stirring the relevant phosphinine with $[(1,5\text{-COD})RhCl]_2$ in dichloromethane (Scheme 2). The formation of a Rh complex was confirmed by $^{31}P\{^1H\}$ NMR spectroscopy in which, in each case, a doublet with a coordination chemical shift of around 10 ppm was observed. The phosphorus-rhodium coupling of around 185 Hz lies between that observed for the analogous $(1,5\text{-COD})RhCl(PPh_3)$ complex ($^1J_{P\text{–}Rh} = 152$ Hz)[19] and that for the $(1,5\text{-COD})RhCl\{P(OPh)_3\}$ complex ($^1J_{P\text{–}Rh} = 273$ Hz).[20] As alluded to above, this appears to suggest that the phosphinines have donor properties that lie somewhere between arylphosphines and arylphosphites. No evidence of a rotational barrier was observed by $^{31}P\{^1H\}$ NMR spectroscopy, presumably due to the complexes being square planar in geometry with a lower steric restriction to P–C rotation than in the $W(CO)_5(L)$ complexes above. The complexes were characterised by NMR spectroscopy with the characteristic reduction in coupling constants for the protons in the C-3 and C-5 positions being observed in the

Table 2 Selected NMR data for **5–8** and their metal complexes

Phosphinine (L)		L	$LW(CO)_5$	LRh(COD)Cl
5	δP	193.1	166.9	186.9
	($J_{P\text{–}Rh}$)			(184.3)
	δH3/5	8.1	8.1	8.1
	($J_{H\text{–}P}$)	(5.9)	(17.4)	(21.5)
	δC2/6	165.3	160.9	(160.0)
	($J_{C\text{–}P}$)	(52.8)	(15.1)	
	δF	−117.2	−113.2	−116.2
6	δP	192.7	164.9	187.5
				(186.3)
	δH3/5	8.0	7.9	8.1
	($J_{H\text{–}P}$)	(6.0)	(17.6)	(15.9)
	δC2/6	168.9	164.6	(157.2)
	($J_{C\text{–}P}$)	(52.8)	15.2()	
7	δP	192.2	165.0	187.3
				(186.3)
	δH3/5	8.0	7.9	7.5
	($J_{H\text{–}P}$)	(6.0)	(17.6)	(7.7)
	δC2/6	168.9	166.5	(147.5)
	($J_{C\text{–}P}$)	(52.7)	(8.8)	
8	δP	192.2	164.9	—
	δH3/5	7.9	7.9	
	($J_{H\text{–}P}$)	(6.2)	(17.6)	
	δC2/6	173.7	170.1	
	($J_{C\text{–}P}$)	(52.8)	(8.8)	

^{1}H NMR spectra as noted for the tungsten complexes above. Unfortunately, the ^{13}C{^{1}H} NMR spectra were not sufficiently well resolved to allow unequivocal assignment of the C-2 and C-6 carbons and only tentative assignments are given in Table 2. The numbering scheme for NMR assignments is given in Fig. 2.

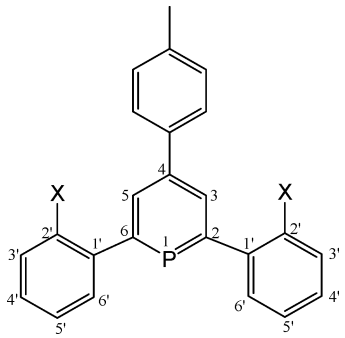


Fig. 2 NMR assignment numbering scheme.

An iodo-phosphinine derivative of the rhodium complex was not obtained as upon addition of the phosphinine to the yellow rhodium dimer solution, the solution immediately turned black. There was no evidence of the desired complex in the ^{1}H NMR spectrum and the ^{31}P{^{1}H} NMR spectrum was silent. No identifiable products could be isolated. This may suggest that the phosphinine underwent cyclometallation at the iodo-(C-2′) position. It is reasonable to propose that C-X oxidative addition might be more facile for the iodo-phosphinine and that this may provide a decomposition pathway. Furthermore, similar behaviour was observed on attempting to coordinate phosphinines **5–8** to a number of palladium(II) precursors. No discrete complexes could be obtained and ^{31}P {^{1}H} NMR spectra of the reaction mixtures were silent. No decomposition products could be identified. Phosphinine–palladium(II) complexes are known,[21] although none have a carbon-halide bond in such an accessible position to the metal as in the current ligands.

Experimental

All compounds were synthesised under nitrogen using standard inert atmosphere (Schlenk) techniques. Compounds **1–4** were obtained and handled as air- and moisture-stable solids. Compounds **5–12** were handled and stored as air- and moisture-sensitive solids while complexes **13–15** were handled as air- and moisture-sensitive compounds for manipulation but were found to be air-stable as solids. All solvents were freshly distilled from sodium or calcium hydride under nitrogen before use. Tris(trimethylsilyl)phosphine was prepared according to a literature route.[22] All other chemicals were of reagent grade and used as supplied unless otherwise stated. The ^{31}P{^{1}H} NMR spectra were recorded on Jeol Eclipse 300 and Bruker DPX500 spectrometers operating at 121.7 and 202.5 MHz respectively, and referenced to 85% H_3PO_4 ($\delta = 0$ ppm). ^{1}H spectra were obtained on a Bruker DPX400 spectrometer (400.8 MHz) or a Bruker DPX500 NMR spectrometer (500.1 MHz) and referenced to tetramethylsilane at $\delta_H = 0$ ppm. ^{13}C{^{1}H} (125.8 MHz) NMR spectra were obtained on a Bruker DPX500 spectrometer and are referenced to tetramethylsilane ($\delta = 0$ ppm). Infrared spectra were recorded either as a solution cell or as Nujol Mulls on a Nicolet 510 FT-IR spectrophotometer. Accurate mass spectra were recorded on a Micromass Q-Tof mass spectrometer calibrated with sodium formate and leucine encephalin as internal standards.

2,6-Bis-(2′-fluorophenyl)-4-tolylpyrylium tetrafluoroborate (1)

Powdered NaOH (1.4 g 36 mmol), 2′-fluoroacetophenone (5 g, 36 mmol) and p-tolylaldehyde (2.2 g, 18 mmol) were mixed together with a pestle and mortar for 25 min. The highly viscous yellow mixture was dissolved in ether (100 ml) and water, the organic phase was separated and washed with water (3 × 50 ml) then brine (3 × 50 ml) and dried over $MgSO_4$. After filtration the solvent was removed in *vacuo* and the resultant crude "diketone" used directly for the synthesis of the pyrylium salt. Thus, under an argon atmosphere, a mixture of "diketone" (950 mg, 1.9 mmol), chalcone (395 mg, 1.9 mmol) and $BF_3.OEt_2$ (7 ml) was stirred at 100 °C for 2 h, then cooled to room temperature and diluted with Et_2O (10 ml). After 12 h the yellow precipitate was filtered off and washed thoroughly with Et_2O to yield 2,6-bis-(2′-fluorophenyl)-4-tolylpyrylium tetrafluoroborate (**1**) as a yellow solid. Yield = 2.8 g (34%). ^{1}H-NMR {$(CD_3)_2CO$}: $\delta = 2.50$ (s, 3H, CH_3), 7.3–7.4 (m, 2H, Ar-H), 7.51 (t, $J = 7.5$ Hz, 4H, Ar-H), 7.7- 7.8 (m, 2H, Ar-H), 8.2–8.3 (m, 2H, Ar-H), 8.01 (d, $J = 8.4$ Hz, 2H, Ar-H), 8.72 (s, 2H, CH 3/5) ppm. ^{13}C{^{1}H}NMR (125.8 MHz; $(CD_3)_2CO$): $\delta = 21.9$, 117.2, 117.7, 117.8, 117.9, 126.4, 129.4, 129.8, 130.7, 131.5, 137.6, 137.7, 149.2, 167.3 ppm. ^{19}F NMR (282.8 MHz, $(CD_3)_2CO$): $\delta = -153.1$ ppm.

2,6-Bis-(2′-chlorophenyl)-4-tolylpyrylium tetrafluoroborate (2)

The synthesis of **2** was identical to that of **1** except that 2′-chloroacetophenone was used. The reaction yielded 2,6-bis-(2′-chlorophenyl)-4-tolypyrylium tetrafluoroborate (**2**) as a yellow solid in 62% yield. ^{1}H-NMR {$(CD_3)_2CO$}: $\delta = 2.58$ (s, 3H, CH_3), 7.6–7.9 (m, 8H, Ar-H), 8.30 (dt, $J = 6.5$, 1.2 Hz, 2H, Ar-H), 8.47 (d, $J = 8.5$ Hz, 2H, Ar-H), 9.15 (s, 2H, CH 3/5) ppm. ^{13}C{^{1}H} NMR (125.8 MHz; $(CD_3)_2CO$): $\delta = 21.9$, 121.2, 129.3, 129.8, 130.6, 131.4, 132.1, 132.5, 134.0, 136.1, 149.6, 167.2, 171.7 ppm.

2,6-Bis-(2′-bromophenyl)-4-tolylpyrylium tetrafluoroborate (3)

The synthesis of **3** was identical to that of **1** except using 2′-bromoacetophenone. The reaction yielded 2,6-bis-(2′-bromophenyl)-4-tolylpyrylium tetrafluoroborate (**3**) as a yellow solid in 89% yield. ^{1}H-NMR (CD_2Cl_2): $\delta = 2.56$ (s, 3H, CH_3), 7.5–7.7 (m, 6H, Ar-H), 7.8–7.9 (m, 2H, Ar-H), 7.9–8.1 (m, 4H, CH 3/5), 8.70 (s, 2H, Ar-H) ppm. ^{13}C{^{1}H} NMR (125.8 MHz; CD_2Cl_2): $\delta = 22.3$, 120.1, 122.3, 129.3, 129.5, 130.4, 130.5, 131.9, 133.3, 135.2, 135.4, 149.9, 166.4, 171.9 ppm.

2,6-Bis-(2′-iodophenyl)-4-tolylpyrylium tetrafluoroborate (4)

The synthesis of **4** was identical to that of **1** except that 2′-iodoacetophenone was used. The reaction yielded 2,6-bis-(2′-iodophenyl)-4-tolylpyrylium tetrafluoroborate (**4**) as a yellow solid in 5% yield. ^{1}H-NMR (CD_2Cl_2): $\delta = 2.53$ (s, 3H, CH_3), 7.2–7.4 (m, 8H, Ar-H), 7.48 (d, $J = 8.2$ Hz, 2H, Ar-H), 7.6–7.7 (m, 2H, Ar-H), 7.89 (dd, $J = 7.8$, 1.5 Hz, 2H, Ar-H), 8.0–8.1 (m, 2H, Ar-H), 8.51 (s, 2H, CH 3/5) ppm. ^{13}C{^{1}H} NMR (125.8 MHz; CD_2Cl_2):

δ = 22.4, 120.3, 129.7, 129.9, 130.6, 132.0, 133.0, 134.5, 135.1, 141.9, 150.1, 166.2, 173.9 ppm.

2,6-Bis-(2′-fluorophenyl)-4-tolylphosphinine (5)

Tris(trimethylsilyl)phosphine (0.84 g, 3.35 mmol, 1.2 equiv.) was added to a slurry of **1** (1.3 g, 2.79 mmol) in DME (40 ml) and the resulting mixture refluxed for 16 h during which time the pyrylium salt dissolved. The DME was then removed in *vacuo* to yield a brown residue. The residue was dissolved in diethyl ether (20 ml), filtered through a pad of neutral aluminium using a further 30 ml of diethyl ether to complete elution of the desired product. The solution was pumped to dryness to yield an orange residue which was crystallised from 40/60 petroleum ether to give 2,6-bis-(2′-fluorophenyl)-4-tolylphosphinine (**5**) as an orange solid. Yield = 0.7 g (56%.). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$): δ = 193.1 ppm. ^1H NMR ($CDCl_3$): δ = 2.29 (s, 3H, CH_3), 7.0–7.2 (m, 6H), 7.23 (m, 2H), 7.42–7.45 (m, 4H), 8.09 (dd, J = 5.9 Hz, 1.5 Hz, 2H, CH 3/5) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 21.3 (s, CH_3), 116.3 (d, J = 22.6 Hz, CH), 124.5 (s, CH), 127.8 (d, J = 18.9 Hz, CH), 129.1 (s, CH), 129.8 (s, CH), 130.9 (dd, J = 0.2, 0.1 Hz, C), 131.7 (dd, J = 13.2, 1.3 Hz, CH), 134.0 (dd, J = 46.5, 2.5 Hz, CH), 138.1 (s, C), 138.9 (d, J = 2.5 Hz, C), 143.1 (d, J = 13.8 Hz, C), 159.1 (dd, J = 246.6, 5.0 Hz, C-2′), 165.3 (d, J = 52.8 Hz, C 2/6) ppm. ^{19}F NMR (282.2 MHz, $CDCl_3$): δ = −117.3 (d, J = 13.9 Hz) ppm. IR (Nujol) cm^{-1}: 1259.8; 1100.5; 1021.6; 802.6; 745.5. Mass Spec. (*m*/*z*): Obs. Mass 375.1119; Calc. Mass 375.1114.

2,6-Bis-(2′-chlorophenyl)-4-tolylphosphinine (6)

Synthesis of **6** was the same as that of **5** except that **2** was used as the pyrylium salt. The reaction gave 2,6-bis-(2′-chlorophenyl)-4-tolylphosphinine **6** as an orange solid in 43% yield. $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$): δ = 192.7 ppm. ^1H NMR ($CDCl_3$): δ = 2.30 (s, 3H, CH_3), 7.0–7.2 (m, 6H), 7.4–7.5 (m, 6 H), 8.02 (d, 2H, J = 6.0 Hz, CH 3/5) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 21.2 (s, CH_3), 127.0 (s, CH), 128.1 (s, CH), 129.4 (s, CH), 129.8 (d, J = 10.1 Hz, CH), 130.2 (s, CH), 132.1 (d, J = 10.1 Hz, CH), 132.4 (d, J = 6.3 Hz, C), 134.1 (d, J = 11.3 Hz, CH), 141.6 (s, C), 141.7 (d, J = 23.9 Hz, C), 142.1 (d, J = 13.8 Hz, C), 147.1 (s, C), 168.9 (d, J = 52.8 Hz, C 2/6) ppm. IR (Nujol) cm^{-1}: 1260.5; 1096.9; 1033.9; 801.9; 756.0. Mass Spec. (*m*/*z*): Obs Mass 407.0514; Calc. Mass 407.0523.

2,6-Bis-(2′-bromophenyl)-4-tolylphosphinine (7)

Synthesis of **7** was the same as that of **5** except that **3** was used as the pyrylium salt. The reaction gave 2,6-bis-(2′-bromophenyl)-4-tolylphosphinine (**7**) as an orange solid in 27% yield. $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$): δ = 192.2 ppm. ^1H NMR ($CDCl_3$): δ = 2.33 (s, 3H, CH_3), 7.1–7.2 (m, 2H), 7.33 (dt, J = 7.5, 0.8 Hz, 2H), 7.42 (d, J = 7.6 Hz, 2H), 7.53 (d, J = 8.1 Hz, 2H), 7.65 (dd, J = 8.0, 0.7 Hz, 2H), 8.02 (d, J = 6.0 Hz, 2H, CH 3/5) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 20.1 (s, CH_3), 126.4 (s, CH), 126.5 (s, CH), 127.2 (s, CH), 128.1 (s, CH), 130.7 (d, J = 10.1 Hz, CH), 132.2 (s, CH), 132.9 (d, J = 11.3 Hz, CH), 136.9 (s, C), 137.6 (s, C), 140.8 (d, J = 13.8 Hz, C), 142.5 (d, J = 22.6 Hz, C), 147.3 (s, C), 168.9 (d, J = 52.7 Hz, C 2/6) ppm. IR (Nujol) cm^{-1}: 1260.3; 1094.2; 1020.7; 801.3. Mass Spec. (*m*/*z*): Obs. Mass 495.9125; Calc Mass 495.9119.

2,6-Bis-(2′-iodophenyl)-4-tolylphosphinine (8)

Synthesis of **8** was the same as that of **5** except that **4** was used as the pyrylium salt. The reaction gave 2,6-bis-(2′-iodophenyl)-4-tolylphosphinine (**8**) as an orange solid in 63% yield. $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$): δ = 192.2 ppm. ^1H NMR ($CDCl_3$): δ = 2.28 (s, 3H, CH_3), 6.95 (t, J = 7.6 Hz, 2H), 7.19 (d, J = 7.9 Hz, 2H), 7.2–7.4 (m, 4H), 7.52 (d, J = 8.1 Hz, 2H), 7.90 (d, J = 6.2 Hz, 2H, CH 3/5) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 20.1 (s, CH_3), 127.6 (s, CH), 128.0 (s, CH), 128.4 (d, J = 16.4 Hz, CH), 129.3 (d, J = 12.6 Hz, CH), 129.8 (s, CH), 130.4 (s, C), 134.0 (d, J = 11.3 Hz, CH), 138.0 (s, C), 138.8 (s, C), 139.7 (d, J = 3.8 Hz, CH), 140.5 (s, C), 147.5 (d, J = 22.6 Hz, C), 173.7 (d, J = 52.8 Hz, C 2/6) ppm. IR (Nujol) cm^{-1}: 1260.1; 1091.9; 1019.7; 800.9. Mass Spec. (*m*/*z*): 590.9257; Calc Mass 590.9236.

[2,6-Bis-(2′-fluorophenyl)-4-tolylphosphinine]-pentacarbonyltungsten(0) (9)

A solution of **5** (0.1 g, 0.27 mmol) in THF was added at room temperature to a solution of $W(CO)_5THF$ (90 mg, 0.27 mmol) in THF. The reaction mixture was stirred at room temperature for 18 h, after which the solution was pumped to dryness. The crude material was washed with 40/60 petroleum ether and the resulting material was recrystallised from 40/60 petroleum ether to give [2,6-bis-(2′-fluorophenyl)-4-tolylphosphinine]pentacarbonyl tungsten(0), **9**, as an orange solid. Yield = 0.12 g (67%). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$): δ = 166.9 (s, $^1J_{P-W}$ = 280.8 Hz) ppm. ^1H NMR ($CDCl_3$): δ = 2.31 (s, 3H, CH_3), 7.1–7.2 (m, 6H), 7.3–7.4 (m, 6H), 7.98 (d, J = 17.4 Hz, 2H, CH 3/5) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 21.3 (s, CH_3), 116.3 (d, J = 21.4 Hz, CH), 124.4 (s, CH), 127.3 (s, CH), 129.0 (t, J = 15.1 Hz, C), 129.9 (s, CH), 130.8 (d, J = 8.8 Hz, C), 132.6 (d, J = 7.5 Hz, CH), 137.2 (d, J = 12.6 Hz, CH), 137.6 (d, J = 5.0 Hz, C), 138.4 (s, C), 140.3 (d, J = 22.6 Hz, C), 159.4 (dd, J = 240.3, 7.5 Hz, C-2′), 160.9 (d, J = 15.1 Hz, C 2/6), 193.8 (d, J = 8.8 Hz, CO), 197.8 (d, J = 32.7 Hz, CO) ppm. ^{19}F NMR (282.2 MHz, $CDCl_3$): δ = −113.2 ppm. IR (hexane) cm^{-1}: 2077.0 (w, CO); 1980.7 (sh, CO); 1958.8 (st, CO); 1260.9; 1101.9; 1016.5; 809.1; 737.8. Mass Spec. (*m*/*z*): 643.0149; Calc Mass 643.0159 (M^+ − 2CO); 614 (M^+ − 3CO); 586 (M^+ − 4CO); 558 (M^+ − 5CO); 375 (L^+).

[2,6-Bis-(2′-chlorophenyl)-4-tolylphosphinine] pentacarbonyltungsten(0) (10)

Compound **10** was made by the same procedure as that for complex **9** except phosphinine **6** was used. The reaction gave [2,6-bis-(2′-chlorophenyl)-4-tolylphosphinine]pentacarbonyltungsten(0), **10**, as an orange solid consisting of two rotamers. Yield = 0.12 g (65%). Major rotamer: $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$): δ = 164.9 (s, $^1J_{P-W}$ = 280.9 Hz) ppm. ^1H NMR ($CDCl_3$): δ = 2.28 (s, 3H, CH_3), 7.13–7.16 (m, 4H), 7.27–7.30 (m, 4H), 7.38–7.44 (m, 4H), 7.93 (d, J = 17.6 Hz, 2H, CH 3/5) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 21.23 (s, CH_3), 126.90 (s, CH), 127.29 (s, CH), 129.91 (s, CH), 130.16 (d, J = 1.3 Hz, CH), 130.37 (s, CH), 132.74 (d, J = 7.5 Hz, CH), 133.67 (d, J = 8.8 Hz, C), 137.08 (d, J = 11.3 Hz, CH), 137.64 (t, J = 6.3 Hz, C), 139.73 (d, J = 12.6 Hz, C), 143.41 (s, C), 147.06 (s, C), 164.62 (d, J = 15.1 Hz, C 2/6), 193.79 (d, J = 8.8 Hz, $^1J_{C-W}$ = 125.5 Hz, *cis*-CO), 197.74 (d, J = 32.7 Hz, *trans*-CO) ppm. IR (hexane) cm^{-1}: 2076.4

(w, CO); 1983.1 (sh, CO); 1954.2 (st, CO); 1261.8; 1171.2; 1147.9; 815.5; 739.7. Minor rotamer (not all peaks were evident): $^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$): δ = 166.6 (s, $^{1}J_{P-W}$ = 280.9 Hz) ppm. ^{1}H NMR ($CDCl_3$): δ = 2.25 (s, 3H, CH_3), 7.13–7.16 (m, 4H), 7.27–7.30 (m, 4H), 7.38–7.44 (m, 4H), 7.90 (d, *J* = 17.5 Hz, 2H, CH 3/5) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 21.13 (s, CH_3), 126.29 (s, CH), 127.03 (s, CH), 129.42 (s, CH), 129.69 (s, CH), 130.09 (s, CH), 132.29 (d, *J* = 7.5 Hz, CH), 133.89 (d, *J* = 8.8 Hz, C), 191.20 (s, CO) ppm. Mass Spec. (*m*/*z*): Obs Mass 674.9567; Calc Mass 674.9554 (M^+ – 2CO); 619 (M^+ – 4CO); 590 (M^+ – 5CO).

[2,6-Bis-(2′-bromophenyl)-4-tolylphosphinine]-pentacarbonyltungsten(0) (11)

Compound **11** was made by the same procedure as that for complex **9** except phosphinine **7** was used. The reaction gave [2,6-bis-(2′-bromophenyl)-4-tolylphosphinine]pentacarbonyl-tungsten(0), **11**, as an orange solid that consists of two rotamers. Yield = 0.1 g (63%). Major rotamer: $^{31}P\{^{1}H\}$ NMR (121.7 MHz, $CDCl_3$): δ = 164.98 (s, $^{1}J_{P-W}$ = 280.8 Hz) ppm. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 2.25 (s, 3H, CH_3), 7.03–7.07 (m, 2H), 7.15 (t, *J* = 7.4 Hz, 2H), 7.21 (t, *J* = 8.4 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.41 (t, *J* = 8.4 Hz, 2H), 7.62 (t, *J* = 8.2 Hz, 2H), 7.92 (d, *J* = 17.6 Hz, 2H, CH 3/5) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 21.44 (s, CH_3), 127.26 (s, CH), 127.49 (s, CH), 128.25 (s, CH), 129.04 (s, CH), 129.89 (t, *J* = 5.0 Hz, CH), 132.57 (d, *J* = 8.8 Hz, CH), 137.13 (d, *J* = 12.5 Hz, CH), 138.32 (s, C), 139.86 (s, C), 141.57 (d, *J* = 13.8 Hz, C), 143.36 (s, C), 148.52 (s, C), 166.52 (d, *J* = 8.8 Hz, C 2/6), 193.76 (d, *J* = 8.8 Hz, *cis*-CO), 197.74 (d, *J* = 32.7 Hz, *trans*-CO) ppm. IR (hexane) cm^{-1}: 2076.4 (w, CO); 1983.1 (sh, CO); 1954.2 (st, CO); 1261.8; 1171.2; 1147.9; 815.5; 739.7. Minor rotamer (some peaks could not be assigned because of overlap): $^{31}P\{^{1}H\}$ NMR (121.7 MHz, $CDCl_3$): δ = 167.21 (s, $^{1}J_{P-W}$ = 280.8 Hz) ppm. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 2.28 (s, 3H, CH_3), 7.62 (t, *J* = 8.1 Hz, 2H), 7.88 (d, *J* = 17.5 Hz, 2H, CH 3/5) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 21.13 (s, CH_3), 127.08 (s, CH), 127.64 (s, CH), 128.18 (s, CH), 130.23 (s, CH), 131.91 (d, *J* = 7.5 Hz, CH), 136.74 (d, *J* = 11.3 Hz, CH), 141.80 (d, *J* = 12.6 Hz, C) ppm. Mass Spec. (*m*/*z*):Obs Mass 819.8140; Calc Mass 819.8159; 736 (M^+ – 3CO).

[2,6-Bis-(2′-iodophenyl)-4-tolylphosphinine]-pentacarbonyltungsten(0) (12)

Compound **12** was made by the same procedure as that for complex **9** except phosphinine **8** was used. The reaction gave [2,6-bis-(2′-iodophenyl)-4-tolylphosphinine]pentacarbonyl-tungsten(0), **12**, as an orange solid that contains two rotamers. Yield = 79 mg (51%). Data was obtained for the major rotamer only. $^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$): δ = 164.9 (s, $^{1}J_{P-W}$ = 280.9 Hz) ppm. ^{1}H NMR ($CDCl_3$): δ = 2.28 (s, 3H, CH_3), 7.13–7.16 (m, 4H), 7.27–7.30 (m, 4H), 7.38–7.44 (m, 4H), 7.93 (d, *J* = 17.6 Hz, 2H, CH 3/5) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 21.22 (s, CH_3), 127.19 (d, *J* = 2.5 Hz, CH), 128.36 (s, CH), 128.50 (s, CH), 129.88 (s, CH), 130.13 (s, CH), 130.50 (s, C), 131.33 (d, *J* = 7.5 Hz, CH), 136.85 (s, C), 137.30 (d, *J* = 12.6 Hz, C), 139.52 (s, CH), 139.76 (s, C), 145.32 (s, C), 170.12 (d, *J* = 8.8 Hz, C 2/6), 193.69 (s, *cis*-CO) ppm. IR (hexane) cm^{-1}: 2076.4 (w, CO); 1983.1 (sh, CO); 1954.2 (st, CO); 1261.8; 1171.2; 1147.9; 815.5; 739.7. Mass Spec. (*m*/*z*): Obs Mass 774.8265; Calc Mass 774.8276 (M^+ – 5CO).

[2,6-Bis-(2′-fluorophenyl)-4-tolylphosphinine]-chloro(COD)rhodium(I) (13)

To a solution of chloro(COD)rhodium(I) dimer (66 mg, 0.13 mmol) in DCM (10 ml) was added phosphinine **5** (0.1 g, 0.27 mmol) in DCM (10 ml). The reaction mixture was allowed to stir at room temperature for 18 h and the solution pumped to dryness. The resultant yellow solid was washed with cold 40/60 petroleum ether and recrystallised from 40/60 petroleum ether to yield [2,6-bis-(2′-fluorophenyl)-4-tolylphosphinine]-chloro(COD)rhodium(I) (**13**) as a yellow solid. Yield = 0.11 g (67%). $^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$): δ = 186.9 (d, *J* = 184.3 Hz) ppm. ^{1}H NMR ($CDCl_3$): δ 1.6–1.7 (m, 4H, COD-aliphatic), 2.04 (m, 4H, COD-aliphatic), 2.33 (s, 3H, CH_3), 3.35 (s, 2H, COD-olefin), 5.42 (s, 2H, COD-olefin), 6.96–7.11 (m, 4H, Ar-H), 7.36 (m, 2H, Ar-H), 7.42 (m, 4H, Ar-H), 8.13 (d, *J* = 14.2 Hz, 2H, CH 3/5), 8.24 (t, *J* = 7.1 Hz, 2H, Ar-H) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 21.2 (s, CH_3), 28.7 (s, COD-aliphatic), 33.0 (s, COD-aliphatic), 71.3 (d, *J* = 12.6 Hz, COD-olefin), 106.4 (s, COD-olefin), 115.7 (d, *J* = 22.6 Hz, CH), 124.3 (s, CH), 127.3 (s, C), 127.5 (s, CH), 128.0 (s, C), 129.8 (s, CH), 130.3 (s, CH), 133.3 (s, CH), 137.2 (s, C), 138.0 (s, CH), 158.1 (s, C), 160.0 (s, C) ppm. ^{19}F NMR (282.8 MHz, $CDCl_3$): δ = –116.6 ppm. IR (Nujol) cm^{-1}: 1260.1, 1091.9, 1020.9, 801.5.

[2,6-Bis-(2′-chlorophenyl)-4-tolylphosphinine]-chloro(COD)rhodium(I) (14)

Complex **14** was synthesised by the same procedure as **13** to yield [2,6,-bis-(2′-chlorophenyl)-4-tolylphosphinine]chloro-(COD)rhodium(I) (**14**) as an orange-yellow solid. Yield = 98 mg (61%). $^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$): δ = 187.5 (d, *J* = 186.3 Hz) ppm. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.71–1.73 (m, 4H, COD-aliphatic), 1.9 (m, 4H, COD-aliphatic), 2.3 (s, 3H, CH_3), 3.4 (s, 2H, COD-olefin), 5.3 (s, 2H, COD-olefin), 7.2 (d, *J* = 8.1 Hz, 4H, Ar-H); 7.3–7.4 (m, 4H, Ar-H), 7.5 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.9 (m, 2H, Ar-H), 8.1 (d, *J* = 15.9 Hz, 2H, CH3/5) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 20.1 (s, CH_3), 28.7 (s, COD-aliphatic), 31.9 (s, COD-aliphatic), 70.4 (d, *J* = 12.6 Hz, COD-olefin), 105.9 (s, COD-olefin), 125.8 (s, CH), 126.4 (s, CH), 127.7 (s, CH), 128.9 (s, CH), 128.7 (s, CH), 128.8 (s, CH), 131.5 (d, *J* = 8.8 Hz, C), 132.7 (s, C), 136.4 (s, C), 137.0 (s, CH), 137.2 (s, C), 146.0 (s, C), 157.2 (s, C) ppm. IR (Nujol) cm^{-1}: 1260.5, 1057.7, 1032.9, 816.6, 758.1.

[2,6-Bis-(2′-bromophenyl)-4-tolylphosphinine]-chloro(COD)rhodium(I) (15)

Complex **15** was synthesised by the same procedure as **13** to yield [2,6-bis-(2′-bromophenyl)-4-tolylphosphinine]chloro(COD)-rhodium(I) (**15**) as an orange-yellow solid. Yield = 76 mg (51%). $^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$): δ = 187.3 (d, *J* = 186.3 Hz) ppm. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.7 (m, 4H, COD-aliphatic), 2.3 (s, 3H, CH_3), 2.4 (m, 4H, COD-aliphatic), 4.2 (s, 2H, COD-olefin), 5.1 (d, *J* = 3.7 Hz, 2H, COD-olefin), 7.07–7.10 (m, 4H, Ar-H), 7.15–7.2 (m, 2H, Ar-H), 7.3 (d, *J* = 8.0 Hz, Ar-H), 7.46 (dd, *J* = 7.7, 1.6 Hz, 2H, CH3/5), 7.49 (d, *J* = 7.3 Hz, 2H, Ar-H) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 20.1 (s, CH_3), 29.9 (s, COD-aliphatic), 40.3 (s, COD-aliphatic), 77.7 (d, *J* = 15.1 Hz, COD-olefin), 104.3 (s, COD-olefin), 125.3 (s, C), 126.2 (s, CH), 127.1 (s, CH), 128.0 (s, C), 128.1 (s, C), 128.3 (s, CH), 128.9 (s, CH),

130.0 (s, CH), 132.2 (s, CH), 135.3 (s, C), 135.5 (s, CH), 142.3 (s, C), 147.5 (s, C) ppm. IR (Nujol) cm^{-1}: 1260.0, 1097.6, 1021.6, 803.8.

Conclusions

We describe a new series of 2-(2′-halo)-substituted phosphinine ligands, and their tungsten and rhodium complexes. We have established the relative σ-donation/π-acceptor abilities of the phosphinines based on comparison of carbonyl stretching frequencies and/or $^1J_{P-W}$ or $^1J_{P-Rh}$ values for the $W(CO)_5(L)$ and (1,5-COD)RhCl(L) complexes with related literature examples. Such comparison suggests that the electronic properties of the halo-arylphosphinines are more like triarylphosphines than phosphites. The dihalo-arylphosphinines are also potentially useful systems for the introduction of other functionalities through substitution of the halides and efforts are ongoing in this vein in an attempt to produce donor functionalised tridentate phosphinines.

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Notes and references

1 P. Le Floch, *Coord. Chem. Rev.*, 2006, **250**(5–6), 627–681; N. Mezailles and P. Le Floch, *Curr. Org. Chem.*, 2004, **10**(1), 3–25.
2 A. R. Hunter, R. J. Whitby, M. E. Light and M. B. Hursthouse, *Tetrahedron Lett.*, 2004, **45**(41), 7633–7636.
3 J. Grundy and F. Mathey, *Angew. Chem Int. Ed.*, 2005, **44**(7), 1082–1084.
4 M. Doux, L. Ricard and P. Le Floch, *Angew. Chem. Int. Ed.*, 2003, **42**(40), 4940–4944.
5 C. Müller and D. Vogt, *Dalton Trans.*, 2007, 5505.
6 M. Doux, N. Mezailles, L. Ricard and P. Le Floch, *Eur. J. Inorg. Chem.*, 2003, **21**, 3878–3894.
7 K. Waschbuesch, P. Le Floch and F. Mathey, *Organometallics*, 1996, **15**(6), 1597–1603.
8 U. Rhorig, N. Mezailles, N. Maigot, L. Ricard, F. Mathey and P. Le Floch, *Eur. J. Inorg. Chem.*, 2000, **12**, 2565–2571.
9 L. Cataldo, S. Choua, T. Berchaz, M. Geoffroy, N. Mezailles, N. Avarvari, F. Mathey and P. Le Floch, *J. Phys. Chem. A*, 2002, **106**(12), 3017–3022.
10 B. Breit, R. Winde, T. Mackewitz, R. Paciello and K. Harms, *Chem. Eur. J.*, 2001, **7**(14), 3106–3121.
11 X. Cheng, S. Hoger and D. Fenske, *Org. Lett.*, 2003, **5**(15), 2587.
12 G. Maerkl, *Angew. Chem.*, 1966, **78**(18–19), 907–908.
13 P. Le Floch, D. Carmichael and F. Mathey, *Organometallics*, 1991, **10**(7), 2432–2436.
14 W. Buchner and W. A. Schlenk, *Inorg. Chem.*, 1984, **23**, 132.
15 W. H. Hersh, P. Xu, B. Wing, J. W. Yom and C. K. Simpson, *Inorg. Chem.*, 1996, **35**, 5453–5459.
16 E. F. Dimauro and M. C. Kozlowski, *J. Chem. Soc., Perkin Trans 1*, 2002, 439.
17 S. O. Grim, D. A. Wheatland and W. McFarlane, *J. Am. Chem. Soc.*, 1967, **89**(22), 5573–5577.
18 G. T. Andrews, I. J. Colquhoun, W. McFarlane and S. O. Grim, *J. Chem. Soc., Dalton Trans.*, 1982, 2353–2358.
19 O. Niyomura, T. Iwasawa, N. Sawada, M. Tokunaga, Y. Obora and Y. Tsuji, *Organometallics*, 2005, **24**, 3468–3475.
20 D. Selent, W. Baumann, R. Kempe, A. Spannenberg, D. Rottger, K. D. Wiese and A. Borner, *Organometallics*, 2003, **22**, 4265–4271.
21 M. Shiotsuka, T. Tanamachi and Y. Matsuda, *Chem. Lett.*, 1995, 531–532.
22 G. Becker, H. Schmidt, G. Uhl and W. Uhl, *Inorg. Synth.*, 1990, **27**, 243.

